Preservation of organics at Mars' near-surface

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CONTEXT AND INTRODUCTION

One of the biggest concerns for the *in situ* detection of organic molecules on extraterrestrial environment is the preservation potential of the molecules at the surface and subsurface given the harsh radiative environment and oxidants they are exposed to.

The Mars Science Laboratory (MSL) mission hosts Sample Analysis at Mars (SAM), a 40 kg suite of instruments which is devoted to make the inventory of organic and inorganic compounds in Mars' atmosphere and subsurface, and understanding their processes of preservation.

To date, SAM has detected and identified several organic molecules in the Martian subsuface, such as chloroalkanes, chlorobenzene at various states of chlorination, sulphur-containaing molecules and functionalized aromatic hydrocarbons.

The presence of organic molecules opens up habitability to another level, where the building blocks of life were available. Understanding their windows of preservation of organics will help in the search for prebiotic or biological signature on Mars.

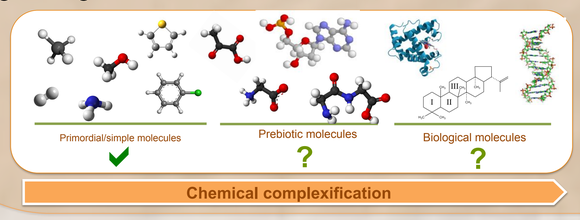
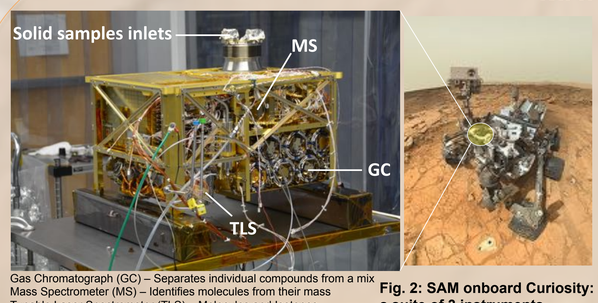


Fig. 1: From chemistry to biology, one can see a complexification of organic molecules. Looking for the whole range will assess the past and present biological potential of Mars.

MATERIAL AND METHODS



Gas Chromatograph (GC) – Separates individual compounds from a mix
Mass Spectrometer (MS) – Identifies molecules from their mass
Tunable Laser Spectrometer (TLS) – Molecules and Isotopes

Fig. 2: SAM onboard Curiosity: a suite of 3 instruments

Fig. 3: MSL traverse map and drilling sites

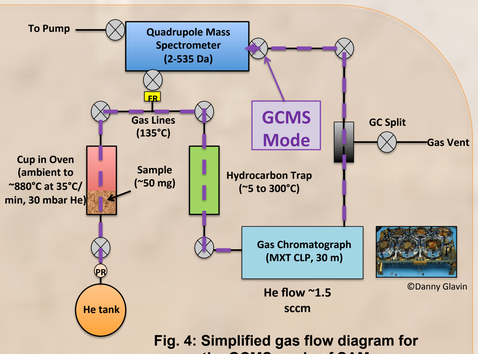
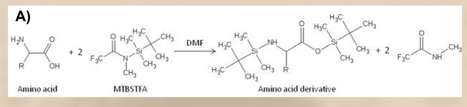


Fig. 4: Simplified gas flow diagram for the GCMS mode of SAM

SAM (Fig. 2) is a suite of three instruments that measure volatiles extracted from solid samples using three primary analytical modes for analysis of organic compounds, including: (1) Evolved gas analysis-quadrupole mass spectrometry (EGA), where solid samples are heated inside a pyrolysis oven up to ~1000°C and the gases released are monitored by quadrupole mass spectrometry (QMS), with portions isolated for gas chromatography mass spectrometry (GCMS) (Fig. 4) and (2) wet chemistry, which consists of an extraction and derivatization with N-methyl-N-tertbutyldimethylsilyl-trifluoroacetamide (MTBSTFA) followed by GCMS anlalysis (Fig. 5).

To date, MSL travelled almost 13 km at the surface of Mars and drilled 10 rocks for 9 SAM analyzes. The two samples discussed in this poster are Cumberland (CB), in the Sheepbed mudstone, and Mojave (MJ), Fine-grained sedimentary deposits in Murray Formation of the Pahrump Hills (Fig. 3).



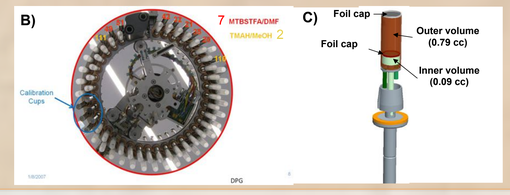
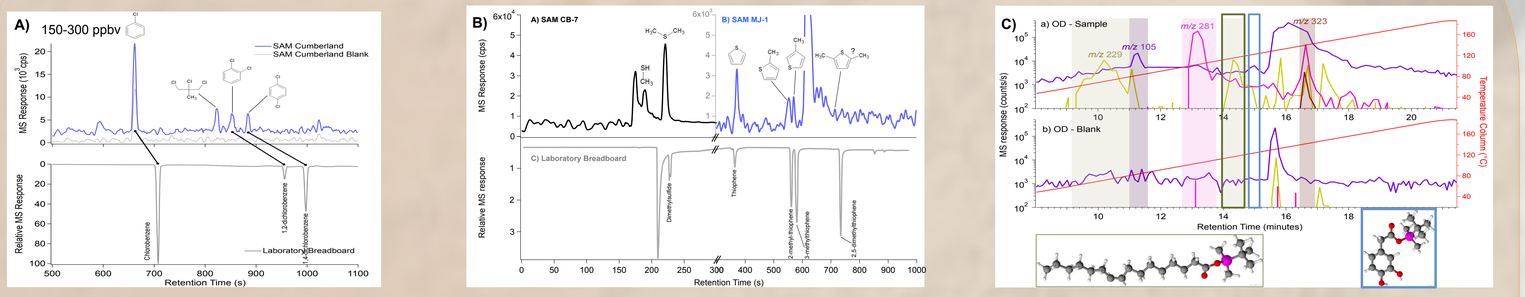


Fig. 5: SAM wet chemistry. A) MTBSTFA derivatization reaction. B) SAM carrousel containing 7 MTBSTFA cups (detailed in C))

RESULTS AND DISCUSSION

1) Detection of organic molecules indigenous to Mars' subsurface

Pyrolysis-GCMS | **Derivatization-GCMS**



Low temperature cut | **High temperature cut**

Fig. 6: SAM GCMS results. A) Low temperature cut on CB sample (< 450 ºC), identification of chlorohydrocarbons from pyrolysis. B) High temperature cut on CB or MJ samples (> 600 ºC), detection of sulfur-containing, non-chlorinated organics from pyrolysis. C) Derivatization GCMS on high temperature cut of CB sample (> 250 ºC), detection of higher complexity, non-chlorinated organics with tentative identification

Several organics were identified on Mars, however, the origin (biological *vs.* abiotic) and the nature of the precursors of the chlorinated organics are unknown (6A).

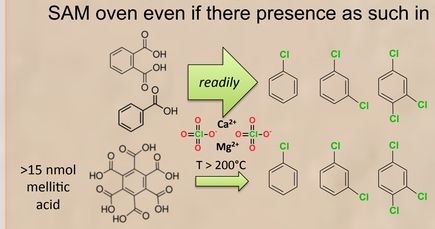
Sulphur-containing compounds identified at high-temperature in CB and MJ (*e.g.* thiophene – 6B). Low-temp organics are chlorinated, high-temp organics are not! High-temp. organics are protected from the O_2/Cl released from the decomposition of perchlorates.

Derivatization (6C) preserves chemical structure enabling identification of possible chlorohydrocarbon precursors and other organics of astrobiological interest (*e.g.* amino/carboxylic acids) that are *not detectable* by pyrolysis GCMS alone.

The first detection of reduced organic compounds in martian near surface samples is a significant step toward understanding the preservation of molecules in oxidative/radiative conditions.

2) Origin of the chlorohydrocarbons – effect of perchlorates

The chlorohydrocarbons are expected to be formed from the reaction of a non-chlorinated precursor present in the sample and Cl from perchlorate decomposition, in SAM oven even if there presence as such in the sample cannot be totally excluded.



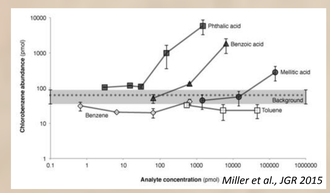


Fig. 7: laboratory experiment show that benzoic, phthalic and mellitic acid, heated in the presence of perchlorate, would form chlorobenzene, dichlorobenzene and trichlorobenzene, and that the abundance of CBZ depends on the initial abundance of the aromatic hydrocarbon.

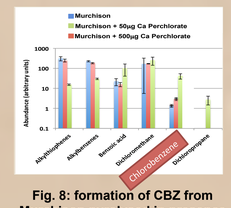


Fig. 8: formation of CBZ from Murchison pyrolysed in presence of perchlorate

Laboratory experiments are integral to Mars results. They show that the organics extract of Murchison meteorites, and that functionalized aromatic hydrocarbons, are good candidates for the formation of chlorobenzene in SAM.

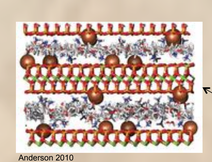
Mellitic acids has been shown (Benner *et al,* PNAS, 2000) to be end-products of decomposition of living systems molecules, and metastable at Mars' surface conditions.

3) Preservation of organics in CB mudstone

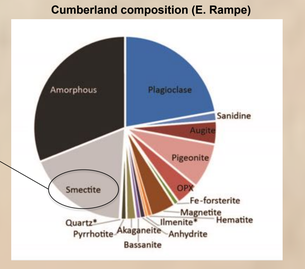
- **Organics are prone to degradation under cosmic radiations. Preserved samples would be buried < 2-3 m**

  CB sample is 65 mm-deep. However, cosmic-ray–produced ^{3}He, ^{21}Ne, and ^{36}Ar yield concordant surface exposure ages of 78 +/- 30 million years (Farley *et al.*, Science, 2014). Recently exposed rocks are good targets for preservation.

- **Clays are good candidates for accumulating and preserving organics over geological timescales**



Anderson 2010



High surface area.
Interlayer charged negatively.
Cation associated with water in the interlayers: retards water flow.

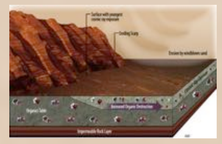
CONCLUSIONS AND PERSPECTIVES

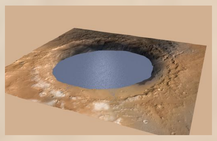
SAM data set + lab experiments are consistent with the presence of organic matter in the sample, with a wider diversity than previously recognized. Organics of martian origin identified in the Sheepbed mudstone and at Parhump Hills can be preserved in the near-surface over geological times!

The presence of perchlorates in the soils does not prevent the detection of organic molecules even if it becomes a powerful oxidant when heated!

Low-temp organics are chlorinated, high-temp organics are not! High-temp. organics are protected from the O_2/Cl released from the decomposition of perchlorates.

SAM data providing important constraints on the types of rock samples (mineralogy, radiation exposition) that should be targeted for future examination and for sample return missions.





Ancient Mars was habitable – was it inhabited?

Lessons learned from SAM derivatization on Mars will feed forward to planning for experiments and wet chemistry on Mars Organic Molecules Analyzer MOMA2020 (ExoMars rover).

MOMA Improvements over SAM:

1) MOMA samples drilled down to 2 meters deep
2) N,N-dimethyl-formamide dimethylacetal (DMF-DMA) derivatization will protect the asymmetrical center(s) of derivatized molecule to discriminate and quantify enantiomers (needs enantiomeric preservation studies)

ACKNOWLEDGEMENTS to all of the MSL and SAM science team, engineers, technical crew, management and support staff at NASA HQ, JPL, NASA Goddard Space Flight Center, the French Space Agency CNES, Honeybee Robotics, UMBC, USRA and other industry partners for making this mission and these SAM measurements possible.